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(54) Title: METHOD FOR THE ELECTROLYTIC POLISHING OF A METAL IN THE PRESENCE OF AN ELECTROLYTE COMPOSITION, AS WELL AS A MOULDED ELEMENT OBTAINED BY USING SUCH A METHOD

(57) Abstract: A method for the electrolytic polishing of a metal in the presence of an electrolyte composition, wherein said metal is a metal selected from the group of gallium, hafnium, antimony, tantalum, titanium, vanadium, aluminium, molybdenum, niobium, tungsten and boron-doped silicon, or an alloy containing one or more of said metals, which metal is subjected to an electrolytic polishing process in an electrolyte composition comprising an inorganic or an organic sulphonic acid compound.

Method for the electrolytic polishing of a metal in the presence of an electrolyte composition, as well as a moulded element obtained by using such a method.

5 The present invention relates to a method for the electrolytic polishing of a metal in the presence of an electrolyte composition, as well as to a moulded element obtained by using such a method.

 The aforesaid method is known per se from US patent no.
10 4,663,005, wherein copper, gold, silver, and alloys of the same are subjected to an electrolytic polishing process by immersing an object made therefrom in an electrolytic solution comprising thiourea, urea, a reducing sugar and an activating acid, and making the object anodic in a DC circuit, wherein the temperature of said electrolytic solution is
15 maintained within the range of 70 - 180 °F and the voltage is maintained at a level of 6 - 12 V. One drawback of such a method is the fact that only metals from Group Ib of the Periodic Table of Elements can be polished in such an electrolytic solution.

 The electrolytic polishing of metal surfaces is also known
20 from US patent 4,148,707, in which patent specification it is stated that a suitable electrolyte solution contains about 55 to about 75% by weight of acids, about 5 to about 15% by weight water, with the remainder by weight consisting of one or more inhibitors, for example aryl sulphonic acids, typically benzene sulphonic acid and toluene sulphonic acid. Only
25 stainless steel is mentioned as a material that can be suitably polished in such an electrolyte composition.

 The electrolytic polishing of tin, tin/lead or other metallic layers of copper-based substrates is known from US patent no. 5,755,950, wherein the electrolyte composition comprises methane
30 sulphonic acid.

 In addition to that, US patents nos. 5,176,803; 5,507,923

and 5,935,411 relate to the electrolytic polishing of specific metals, in particular tungsten, molybdenum, silicon and platinum.

French patent application no. 2 467 248 discloses a special electrolyte composition that is used for the electrochemical polishing of titanium and titanium alloys, comprising an aqueous solution of sulphuric acid, nitric acid, hydrofluoric acid and a surfactant, viz. a mixture of the sodium salt of an alpha sulphonic carbonic acid comprising 17 - 20 carbon atoms and the sodium salt of a carbonic acid comprising 17 - 20 carbon atoms.

International patent application WO 99/00537 discloses a method for electrochemically removing an electrically non-insulating part, for example molybdenum as the metal, from a structure by exposing said structure to an acidic electrolyte composition comprising an organic solvent, for example dimethyl sulfoxide, and a sulphonic acid, for example an aromatic sulphonic acid, such as paratoluene sulphonic acid.

Japanese patent publication no. 03 053099 discloses a method for selectively etching tantalum by means of an electrolytic process, using an electrolyte composition comprising a sulphonic acid group and an sulphonate group.

Russian patent publication no. 670 607 discloses a method for electropolishing metals, for example Mo-Re alloys, wherein an aqueous solution containing sulphuric acid, phosphoric acid, carboxymethyl cellulose and a salt of butyl naphtalene sulphonic acid is used.

From Japanese patent publication no. 60 092500 there is known an electrolyte composition for electropolishing a niobium material, which aqueous electrolyte composition consists of concentrated sulphuric acid and fluorosulphuric acid.

Japanese patent publication no. 61 076699 discloses the anodic oxidation of aluminium or an aluminium alloy in an aqueous solution containing chromic acid and one or more types of compounds selected from the group of sulphonic acid, sulphonates, sulphamic acid

and sulphamates.

US patent no. 4,194,954 discloses the electrolytic etching of surfaces of semiconductor materials, for example InSb, GaAs and InAs, wherein a two-component electrolyte composition is used.

5 The object of the present invention is to provide a method for electropolishing a metal in the presence of an electrolyte composition, wherein in particular one or more elements selected from the groups of IVb, Vb and VIb and possibly combinations of elements from groups IIIa and Va of the Periodic Table of Elements can be used.

10 Another object of the present invention is to provide a method for electropolishing a metal in the presence of an electrolyte composition, wherein a quick and efficient electrolysis provides a smooth surface or shapes a moulded element.

15 According to the invention, the method as referred to in the introduction is characterized in that said metal is a metal selected from the group of gallium, hafnium, antimony, tantalum, titanium, vanadium, aluminium, molybdenum, niobium, tungsten and boron-doped silicon, or an alloy containing one or more of said metals, which metal is subjected to an electrolytic polishing process in an electrolyte
20 composition comprising an inorganic or an organic sulphonic acid compound. In addition, suitable metals for use in the present method are combinations of elements from group IIIa with elements from group Va of the Periodic Table of Elements, as well as metals from the series of lanthanides, including lanthanum.

25 Although the electrolytic polishing of a zirconium and/or a zirconium alloy in an electrolyte composition is known from German Patentschrift no. 33 02 011, the use of the aforesaid metals is neither disclosed nor suggested therein. In addition to that, the polishing of a surface of an oxide composition with a base of tantalum is known from
30 Japanese patent publication no. 06249771, wherein an etching solution consisting of nitric acid and hydrofluoric acid having a temperature of

100 °C or higher is used. The use of a sulphonic acid compound, which may or may not be organic, in an anodic etching process at a low temperature is not known therefrom, however. Although an aryl sulphonic acid-containing electrolyte composition for electrolytic polishing is known
5 from the aforementioned US patent no. 4,148,707, the aforesaid group of metals and/or alloys as the material to be polished is not known therefrom. Although Piotrowski, O., Madore, C. and Landolt, D. have described the use of an electrolyte composition consisting of sulphuric acid-methanol for electropolishing tantalum in *Electrochim. Acta* (1999),
10 44(19), 3389-3399, it has become apparent that such an electrolyte solution does not produce a sufficiently smooth tantalum surface.

The term "electrolytic polishing" as used in this introduction to the description is to be understood to comprise the anodic dissolution of a metal in a suitable electrolyte solution. In the
15 literature such a method of electrolytic polishing is also called electrochemical polishing or electropolishing, which designations can be considered to be synonyms. In addition to that, the term electrolytic polishing is to be understood to include the cutting or shaping of materials and the anodic dissolution of materials, such as
20 electrochemical etching or drilling.

The electrolytic polishing of a metal, or of an alloy containing a metal belonging to the present group takes place in an electrolytic cell, wherein the metal to be dissolved is anodically connected. Using an external voltage source, a specific potential is
25 applied, so that the oxidation reaction takes place on the material to be polished (the anode). During this process, the electrons of the material are transported from the anode side to the cathode side, using an external circuit. Since the anode material releases electrons, the material is ionized and go into solution while forming complexes with
30 suitable anions or form a precipitate. The reduction reaction takes place at the cathode side. In an acidic environment the hydrogen ions will be

reduced at the cathode side while forming hydrogen gas. Electrolytic polishing has the advantage that it can readily be used with workpieces having complex geometries and/or small dimensions. In addition, the workpiece is not subjected to thermal or mechanic loads.

5 Experiments carried out by the present inventors have shown that an electrolytic polishing process is preferably carried out when the rate of dissolution of the metal, or of an alloy containing one or more metals, is mass transport limited. Under these conditions the primary current distribution is less important, as a result of which the surface
10 will dissolve more uniformly and consequently will look smooth. The term "mass transport limited situation" as used above is to be interpreted as the situation that is reached when the current density no longer increases while the voltage continues to rise. In a so-called current-voltage curve (also called iE -curve), this is represented by a platform
15 of a constant current density, which value is called the limiting current.

It is in particular preferred when carrying out the present method to use tantalum as the metal, for which metal no suitable treatment for obtaining a smooth and uniform surface has been available
20 so far.

It is in particular preferred when carrying out the method according to the present invention to use an organic alkane sulphonic acid compound or a salt thereof in a mixture with one or more aliphatic alcohols according to formula $C_nH_{2n+1}OH$, wherein $n = 1-4$, as the
25 electrolyte composition, whereby it is especially preferred to use methane sulphonic acid, ethane sulphonic acid, trifluoromethane sulphonic acid or a mixture thereof as said organic alkane sulphonic acid compound.

According to another preferred embodiment of the present invention, an aromatic organic sulphonic acid compound or a salt thereof
30 in a mixture with one or more aliphatic alcohols according to formula $C_nH_{2n+1}OH$, wherein $n = 1-4$, is used as the electrolyte composition, whereby

it is especially preferred to use paratoluene sulphonic acid, benzene sulphonic acid or a mixture thereof as said aromatic organic sulphonic acid compound.

5 It is possible to use one or more compounds from the group of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, isobutanol, tertiary butanol and isoamyl alcohol as a suitable aliphatic alcohol compound.

10 The specific selection of the aliphatic alcohol compound is in particular connected with the conductivity of the electrolyte solution. If in the formula $C_nH_{2n+1}OH$, wherein $n = 1-4$, parameter n has a value of more than 4, the conductivity will be undesirably reduced, which has an adverse effect on the present method for electrolytic polishing.

15 In a special embodiment of the present invention it is preferred to use an inorganic sulphonic acid compound, preferably fluorosulphonic acid or trifluoromethane sulphonic acid, or a salt thereof in a mixture with one or more aliphatic alcohols according to the formula $C_nH_{2n+1}OH$, wherein $n = 1-4$, as the electrolyte composition.

20 In specific embodiments it is preferred to use the (an)organic sulphonic acid compound in the electrolyte composition in combination with dimethyl sulphoxide (DMSO) and/or ethylene glycol instead of with the aforesaid aliphatic alcohol.

It is in particular preferred for the proportion of inorganic or organic sulphonic acid compound to be > 1 vol.%, preferably 1 - 90 vol.%, of the total amount of electrolyte composition.

25 If the aforesaid proportion is lower than the minimum of 1 vol.%, the rate at which the metal, or an alloy containing one or more metals, goes into solution is low for practical applications, which is mainly caused by the low conductivity of the overall electrolyte composition. Moreover, a proportion of more than 90 vol.% is undesirable, 30 owing to a disadvantageous increase of the viscosity of the electrolyte composition in addition to the specific conductivity.

In order to prevent an oxide film from being formed on the metal surface anew during the electrolytic polishing process, the electrolyte composition that is used preferably has a water content of 0 - 10 vol.%.

5 In a specific embodiment it is furthermore preferred for the electrolyte composition to comprise one or more surfactants.

The present invention furthermore relates to a moulded element which is made of a metal and/or an alloy obtained by using the present method, which moulded element is in particular suitable for use
10 in biomedical applications, preferably in a stent that is to be implanted into the human body. Such a moulded element must have a very smooth surface and be free from impurities, which aspects are realised in an outstanding manner by using the present method.

The present invention will be explained in more detail
15 hereafter by means of an example, whereby it should be noted, however, that the present invention is by no means limited to such a specific example.

Example.

All experiments were carried out in an electro-chemical
20 cell, using a computer-controlled potentiostat (Autolab A, Eco Chemie). The anode, that is, the material to be subjected to an electropolishing process, is a rotary disc electrode. Such a rotary disc electrode is a flat disc made of the metal to be dissolved, which disc is rotated at a special rotational speed. Mercury/mercury sulphate was disposed under the
25 rotary disc electrode, at a distance of 0.5 ± 0.2 cm therefrom, as a reference electrode. All experiments were carried out at room temperature. In the appended table the experimental data are shown, with the anode being referred to as substrate.

Table

Data relating to electrolytic polishing process													
Substrate	Electrolyte composition	Weight fraction acid	Volume fraction acid	Weight fraction water	Volume fraction water	p (25°C) [g.cm ⁻³]	E vs RE [V]	Rotation speed [rpm]	Duration [s]	Charge [C]	Reduction [mg]	Anodic rate of dissolve	Performance of electrolytic polishing process
1 Titanium	MSA/m	0.65	0.50	0.012	0.0144	1.2	8	0.4	25	200	31.4	3.5	Good
2 Aluminium alloy 5050	MSA/m	0.65	0.50	0.012	0.0144	1.2	2	0.35	25	x	x	Good	Extremely good
3 Molybdenum	MSA/m	0.65	0.50	0.012	0.0144	1.2	8	0.85-0.97	25	300	106.1	16	Good
4 Tantalum	MSA/m	0.81	0.69	0.016	0.016	1.2	8	0.1	25	400	41.4	15	Extremely good
5 Tantalum	MSA/m	0.65	0.50	0.012	0.0144	1.2	8	0.6	25	200	46.1	17	Extremely good
6 Tantalum	MSA/m	0.45	0.30	0.009	0.00972	1.08	8	1.66-1.94	25	200	139.7	52	Extremely good
7 Tantalum	MSA/m	0.27	0.16	0.005	0.00505	1.01	8	2.21-2.42	25	100	88.7	33	Extremely good
8 Tantalum	MSA/m	0.2	0.12	0.004	0.004	1.01	8	> 3	25	50	53.5	7.5	Extremely good
9 Tantalum	MSA/m	0.1	0.06	0.002	0.002	1.01	8	2.5	25	200	50.3	7.3	Moderate
10 Tantalum	MSA/m	0.02	0.01	0.0005	0.0005	1.01	8	0.6	25	200	50.3	7.3	Moderate
11 Tantalum	FSAlm	0.1	0.06	0.004	0.004	1.01	8	0.1-0.5	10/m64	300	30.9	11	Extremely good
12 Tantalum	MSAlm	0.81	0.46	0.01	0.01	1.2	8	0.1-0.5	10/m64	300	30.9	11	Extremely good
13 Tantalum	MSA/m	0.65	0.50	0.035-0.045	0.048	1.2	8	0	25	x	0	No	Moderate
14 Boron doped silicon	MSA/m	0.65	0.50	0.012	0.0144	1.2	10	0	200	7	7	Pitting	No
15 G3Sb	BSA/m	0.25	0.50	0.012	0.0144	1.2	8	0	0	0	0	Good	Good
16 Super alloy (Ni,Ti,Al, Cr)	MSA/m	0.65	0.50	0.012	0.0144	1.2	>	0.7	0	75	7	Good	Good
17 stainless steel	MSA/m	0.27	0.16	0.005	0.00505	1.01	8	0	0	0	0	Extremely good	Extremely good
18 Vanadium	MSA/m	0.27	0.16	0.005	0.00505	1.01	8	0	0	0	0	Extremely good	Extremely good
19 Niobium	MSA/m	0.27	0.16	0.005	0.00505	1.01	8	0	0	0	0	Extremely good	Extremely good
20 Tungsten	MSA/m	0.27	0.16	0.005	0.00505	1.01	8	0	0	0	0	Extremely good	Extremely good
21 Tantalum	p-TSA/m	0.4	0.4	0.042	0.0432	0.96	8	1.1-2	25	250	148	7	Extremely good
22 Tantalum	p-TSA/m	0.65	0.50	0.06	0.0612	1.02	8	0.21	25	500	43	13.5	Extremely good
23 Tantalum	H ₂ SO ₄ /m	0.22	0.11	0.01	0.0096	0.96	7	0.35	25	300	39.4	15	Extremely fair
24 Tantalum	H ₂ SO ₄ /m	0.55	0.35	0.023	0.0096	0.96	10	0	25	x	0	No	No
25 Tantalum	MSAIDMSO	0.46	0.39	0.023	0.0096	0.96	9.5	0.1	25	1000	148	15	Extremely fair
26 Tantalum	MSAIEG	0.26	0.21	0.023	0.0096	0.96	10	0.4	25	100	148	15	Extremely fair
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It is apparent from the table that the electrolyte composition that is used for electrolytic polishing is a decisive factor as regards the quality of the metal that is eventually obtained. Subjecting tantalum to an electrolytic polishing process in a mixture of sulphuric acid and methanol (see example 23) provides a tantalum surface which can be defined as rather mediocre. From the table it can furthermore be clearly concluded that a superalloy consisting of nickel, tantalum, aluminium and chromium (see example 16) can be suitably subjected to an electrolytic polishing process, using an electrolyte solution consisting of methane sulphonic acid.

CLAIMS

1. A method for the electrolytic polishing of a metal in the presence of an electrolyte composition, characterized in that said metal
5 is a metal selected from the group of gallium, hafnium, antimony, tantalum, titanium, vanadium, aluminium, molybdenum, niobium, tungsten and boron-doped silicon, or an alloy containing one or more of said metals, which metal is subjected to an electrolytic polishing process in an electrolyte composition comprising an inorganic or an organic
10 sulphonic acid compound.
2. A method according to claim 1, characterized in that tantalum is used as said metal.
3. A method according to claims 1 - 2, characterized in that an organic alkane sulphonic acid compound or a salt thereof in a mixture
15 with one or more aliphatic alcohols according to formula $C_nH_{2n+1}OH$, wherein $n = 1-4$, is used as said electrolyte composition.
4. A method according to claim 3, wherein methane sulphonic acid, ethane sulphonic acid, or a mixture thereof is used as said organic alkane sulphonic acid compound.
- 20 5. A method according to claims 1 - 2, characterized in that an aromatic organic sulphonic acid compound or a salt thereof in a mixture with one or more aliphatic alcohols according to formula $C_nH_{2n+1}OH$, wherein $n = 1-4$, is used as said electrolyte composition.
6. A method according to claim 5, characterized in that
25 paratoluene sulphonic acid, benzene sulphonic acid or a mixture thereof is used as said aromatic organic sulphonic acid compound.
7. A method according to claims 1 - 2, characterized in that an inorganic sulphonic acid compound or a salt thereof in a mixture with one or more aliphatic alcohols according to the formula $C_nH_{2n+1}OH$, wherein
30 $n = 1-4$, is used as said electrolyte composition.
8. A method according to claim 7, characterized in that

fluorosulphonic acid or trifluoromethane sulphonic acid is used as said inorganic sulphonic acid compound.

9. A method according to claims 3 - 8, characterized in that one or more compounds from the group of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, isobutanol, tertiary butanol and isoamyl alcohol are used as the aliphatic alcohol compound.

10. A method according to claims 1 - 8, characterized in that the aliphatic alcohol in the electrolyte composition is substituted for one or more compounds from the group of dimethyl sulphoxide and ethylene glycol.

11. A method according to claims 1 - 10, characterized in that the proportion of inorganic or organic sulphonic acid compound is > 1 vol.% of the total amount of electrolyte composition.

12. A method according to claim 11, characterized in that the proportion of inorganic or organic sulphonic acid compound is 1 - 90 vol.% of the total amount of electrolyte composition.

13. A method according to claims 1 - 12, characterized in that the electrolyte composition that is used has a water content of 0 - 10 vol.%.

14. A moulded element made of a metal and/or an alloy obtained by using the method as defined in claims 1 - 13, which moulded element is intended for use in biomedical applications.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 01/00220

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C25F3/16 C25F3/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C25F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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